

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-086243

(43)Date of publication of application : 20.03.2003

(51)Int.Cl.

H01M 10/40

H01M 4/02

H01M 4/58

(21)Application number : 2001-270548

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(22)Date of filing : 06.09.2001

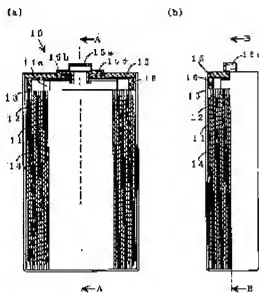
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## (54) MANUFACTURING METHOD OF NONAQUEOUS ELECTROLYTIC SOLUTION SECONDARY BATTERY AND NONAQUEOUS ELECTROLYTIC SOLUTION SECONDARY BATTERY

(57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a nonaqueous electrolytic solution secondary battery in which generation of battery swelling can be suppressed even if vinylene carbonate is made to be dissolved in the electrolytic solution and even if cycle characteristics have been improved.

**SOLUTION:** This manufacturing method of this nonaqueous electrolytic solution secondary battery has been made to be provided with a vinylene carbonate dissolving process in which the vinylene carbonate is made to be dissolved in the nonaqueous electrolytic solution, a carbon dioxide gas dissolving process in which carbon dioxide gas is made to be dissolved and made to exist in the nonaqueous electrolytic solution wherein the vinylene carbonate has been dissolved, and a solution-injecting process in which the nonaqueous electrolytic solution into which the vinylene carbonate has been dissolved and the carbon dioxide gas has been made to be dissolved and made to exist in the



nonaqueous electrolytic solution is injected into a sheath can 14. By this, oxidative degradation of the vinylene carbonate dissolved in the electrolytic solution becomes to be suppressed by the effect of the coatings formed by these carbon dioxide gas and vinylene carbonate. As a result, even if the nonaqueous electrolytic solution secondary battery 10 is left out at high-temperatures, the battery swelling is obstructed.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]The negative electrode containing the negative electrode active material which consists of a carbon material for which this invention can be desorbed [ insertion and ] from a lithium ion, It is related with the manufacturing method of the nonaqueous electrolyte secondary battery provided with the separator which isolates the anodes containing the positive active material in which the insertion and desorption from a lithium ion are possible, and these anodes and negative electrodes, and nonaqueous electrolyte in the armor can, and the nonaqueous electrolyte secondary battery manufactured by this manufacturing method.

[0002]

[Description of the Prior Art]In recent years, the nonaqueous electrolyte secondary battery which has a small light weight and is represented with high capacity with a lithium secondary battery as a chargeable and dischargeable cell comes to be put in practical use, and it came to be used for a portable electron, communication equipment, etc., such as a small video camera, a cellular phone, and a notebook computer. The carbon system material in which the insertion and desorption from a lithium ion are possible is used for this kind of lithium secondary battery as negative electrode active material, Lithium containing transition metal oxides, such as  $\text{LiCoO}_2$  [ in which the insertion and desorption from a lithium ion are possible ],  $\text{LiNiO}_2$ , and  $\text{LiMn}_2\text{O}_4$ , and  $\text{LiFeO}_2$ , are used as positive active material, It is a rechargeable battery constituted using the nonaqueous electrolyte which dissolved the solute which consists of lithium salt in the organic solvent.

[0003]By the way, on the carbon system material used for the negative electrode of such a lithium secondary battery, nonaqueous electrolyte involves and the side reaction which has an adverse effect on a battery characteristic arises. For this reason, while forming a tunic in a negative electrode surface so that the negative electrode (carbon negative electrode) which

consists of carbon system materials may not carry out a direct reaction to an organic solvent, it has been an important technical problem to control the formed state and character of this tunic. The art which generally adds a special additive agent in an electrolysis solution as art which controls such a negative electrode surface tunic (SEI:Solid ElectrolyteInterface) is known. He adds to the nonaqueous electrolyte which dissolved the typical solute which vinylene carbonate (it is called VC below by VC:) is known, and becomes an organic solvent from lithium salt about this VC if an additive agent is carried out, and is trying to use.

[0004]

[Problem(s) to be Solved by the Invention]If the electrolysis solution in which VC mentioned above was added is used for a lithium secondary battery, SEI will be formed on the surface of a carbon negative electrode, the side reaction in which the nonaqueous electrolyte on a carbon negative electrode participates will be inhibited, and a cycle characteristic will improve.

However, the lithium secondary battery using the electrolysis solution in which VC was added produced the problem that cell bulging occurred at the time of high temperature preservation. If the lithium secondary battery using the electrolysis solution in which VC was added is neglected at an elevated temperature, oxidative degradation of the VC will be carried out, this will generate carbon dioxide, and it will be guessed that it is what cell bulging produced. In the square-shaped cell which made thickness of the armor can thin, especially the problem of this cell bulging becomes remarkable, in order to realize high energy density. And if cell bulging arises, the cell case (case of a battery pack where a protection circuit and two or more cells were stored) which has stored this cell will also blister, and fitting with the electronic equipment equipped with a cell case will come to cause fault, such as worsening.

[0005]Then, when this invention persons made carbon dioxide dissolved in the nonaqueous electrolyte in which such VC was added as a result of examining many things about a restraint means which does not produce cell bulging, even if it added VC to nonaqueous electrolyte, they acquired the knowledge that cell bulging could be controlled. This invention was made based on such knowledge, and is \*\*\*\*. even if the purpose is alike, adds VC and raises a cycle characteristic, it is providing the manufacturing method of the nonaqueous electrolyte secondary battery which can control generating of cell bulging.

[0006]

[Means for Solving the Problem]In order to attain the above-mentioned purpose, a manufacturing method of a nonaqueous electrolyte secondary battery of this invention, A vinylene carbonate melting process which dissolves vinylene carbonate (VC) in nonaqueous electrolyte, He is trying to have a pouring-in process of pouring in nonaqueous electrolyte in which a carbon dioxide dissolved process in which carbon dioxide is made dissolved, and VC were dissolved in nonaqueous electrolyte in which VC was dissolved, and carbon dioxide was

dissolved in an armor can.

[0007] Thus, if nonaqueous electrolyte in which VC was dissolved and carbon dioxide was dissolved is poured in in an armor can, carbon dioxide will contact a carbon material used as negative electrode active material, and a coat of carbonic acid will come to be formed on the surface of a negative electrode. If this is charged, a tunic of organic carbonic acid will be formed on the surface of a negative electrode of VC. Then, even if it saves this nonaqueous electrolyte battery at an elevated temperature (neglect), it can control that oxidative degradation of the VC is carried out by operation of these tunics. As a result, even if it saves a nonaqueous electrolyte secondary battery at an elevated temperature (neglect), generating of cell bulging can be controlled.

[0008] And when making carbon dioxide dissolved in nonaqueous electrolyte in which VC was dissolved, it is desirable that you make it dissolved until carbon dioxide is saturated in nonaqueous electrolyte. In this case, it is preferred that you make it dissolved in it until carbon dioxide is saturated with ordinary temperature ordinary pressure in nonaqueous electrolyte in which VC was dissolved by what carbon dioxide is blown for (bubbling is carried out). Here, if content of VC exceeds 5.0 mass % to mass of nonaqueous electrolyte, initial capacity of a cell will fall. On the contrary, if content of VC becomes less than 0.1 mass % to mass of an electrolysis solution, an effect of preventing degradation by a reaction with nonaqueous electrolyte will decrease. For this reason, as for content of VC dissolved in nonaqueous electrolyte, it is desirable to use 0.1 - 5.0 mass % to mass of nonaqueous electrolyte.

[0009] As a carbon material which constitutes a negative electrode, if a spacing ( $d_{002}$ ) of a field (002) is a carbon material (black lead) of 0.340 nm or less, It became clear by experiment that initial service capacity is large, and excel in a cycle characteristic and a nonaqueous electrolyte secondary battery with little cell bulging at the time of high temperature preservation is obtained. For this reason, it can be said that it is preferred that a spacing ( $d_{002}$ ) of a field (002) uses 0.340 nm or less of black lead as a carbon material which constitutes a negative electrode. This invention can be used without restricting about a kind of positive active material or nonaqueous electrolyte. For example, as positive active material,  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ , and  $\text{LiMn}_2\text{O}_4$  etc. are preferred on a metallic oxide and a concrete target containing manganese, cobalt, and at least one sort of nickel.

[0010]

[Embodiment of the Invention] Below, an embodiment of the invention is described.

1. Nonaqueous electrolyte secondary battery drawing 1 shows the nonaqueous electrolyte secondary battery by this invention, the negative electrode plate 11 and the anode board 12 wound this nonaqueous electrolyte secondary battery 10 spirally via the separator 13, and it is stored and provided with the electrode group made into flat shape in the square-shaped armor

can 14. the upper opening of this armor can 14 -- the obturation object 15 -- liquid -- it obturates densely. and the negative electrode lead 11a which extended from the negative electrode plate 11 -- the obturation object 15 -- the insulator 15b -- passing -- it is connected to the closed tag block 15c.

[0011]After pouring in an electrolysis solution from the bore provided in the tag block 15c, it is made as [ close / weld the negative pole terminal 15a to the tag block 15c, and / a bore ]. The outermost periphery of the electrode group is arranged without applying positive electrode mixture (anode slurry) to both sides of the positive pole collector which consists of aluminium foil. A part of upper bed part of this positive pole collector is started, it is made into a positive electrode lead (not shown), puts this positive electrode lead between the armor can 14 and the obturation object 15, and is connected to the armor can 14 which serves as a positive pole terminal by laser welding. The spacer 16 is arranged between the electrode group and the obturation object 15, and the electrode group is held in the armor can 14 by this spacer 16.

[0012]Here, the separator 13 is formed from the fine porous membrane made from polyethylene. The armor can 14 carries out press working of sheet metal of the aluminum alloy, and is fabricating it in the square shape. The obturation object 15 also carried out press working of sheet metal of the aluminum alloy, and fabricated it, and it has the negative pole terminal 15b via the insulator 15b. In order to consider it as the nonaqueous electrolyte secondary battery of high energy density, Although the construction material of the armor can 14 and the obturation object 15 has a preferred aluminum alloy, it is not limited to this and aluminum, iron, nickel, titanium, magnesium, etc. and the alloy that made these metal the subject can be suitably used according to battery construction. The safety valve which is not illustrated is provided in this obturation object 15, and if gas is emitted and internal pressure rises in a cell, it is made as [ emit / the emitted gas / out of a cell ]. Below, the production procedures of the nonaqueous electrolyte secondary battery 10 constituted in this way are explained in detail.

[0013]2. In production \*\*\*\* of the production (1) negative electrode plate of a nonaqueous electrolyte secondary battery, and the spacing ( $d_{002}$ ) of the field (002), the size ( $L_c$ ) of the microcrystal of c shaft orientations prepared the powder of massive black lead (artificial graphite calcinated at 2950 \*\*) whose mean particle diameter is 20 micrometers in 200 nm at 0.336 nm. Subsequently, after making water distribute the dispersion (solid content is 48 mass %) of this graphite powder and the styrene butadiene rubber (SBR) as a binder, carboxymethyl cellulose (CMC) used as a thickener was added, it mixed, and the negative-electrode slurry was prepared. It prepared so that the mass composition ratio after desiccation with massive black lead, and SBR and CMC might be set to massive black lead:SBR:CMC=95:3:2.

[0014]It replaces with a styrene butadiene rubber (SBR) as a binder, Ethylenic-unsaturated-carboxylic-acid ester, such as methyl (meta) acrylate, ethyl (meta) acrylate, butyl (meta)

acrylate, acrylonitrile (meta), and hydroxyethyl (meta) acrylate, may be used. Or ethylenic unsaturated carboxylic acid, such as acrylic acid, methacrylic acid, itaconic acid, fumaric acid, and maleic acid, may be used. As a thickener, it may replace with carboxymethyl cellulose (CMC) and methyl cellulose, hydroxymethylcellulose, ethyl cellulose, polyvinyl alcohol, polyacrylic acid (salt), oxidation starch, phosphorylation starch, casein, etc. may be used. [0015] Subsequently, the negative pole collector which consists of copper foil was prepared,  $100 \text{ g/m}^2$  was applied to both sides of this negative pole collector for the negative-electrode slurry produced as mentioned above with the doctor blade method per unit area of a negative pole collector, and the negative electrode active material layer was formed. Then, after carrying out vacuum drying at  $100^\circ\text{C}$  for 2 hours, it rolled so that the pack density of a graphite material might become  $1.6 \text{ g/cm}^3$ , and it cut in predetermined shape, and the band-like negative electrode plate 11 was produced. It extends from the end part of the negative electrode plate 11, and the negative electrode lead 11a is formed.

[0016] (2) Cobalt-acid-lithium ( $\text{LiCoO}_2$ ) powder with a production mean particle diameter of 5 micrometers of an anode board and the artificial-graphite powder as a conducting agent were mixed at a rate of 9:1 with the mass ratio, and positive electrode mixture was prepared. This positive electrode mixture and the binder solution which did the 5 mass % dissolution of polyvinylidene fluoride (PVdF) at N-methyl-2-pyrrolidone (NMP) were kneaded so that it might be set to 95:5 with the mass ratio of solid content, and the anode slurry was prepared. [0017] Subsequently, the positive pole collector which consists of aluminium foil was prepared,  $240 \text{ g/m}^2$  was applied to both sides of a positive pole collector for the anode slurry produced as mentioned above with the doctor blade method per unit area of a positive pole collector, and the positive electrode mixture layer was formed. Then, after carrying out vacuum drying at  $150^\circ\text{C}$  for 2 hours, it rolled so that the pack density of positive electrode mixture might become  $3.2 \text{ g/cm}^3$ , and it cut in predetermined shape, and the band-like anode board 12 was produced. In the anode board 12, an anode slurry is not applied to the portion arranged at an outermost periphery at the time of winding, but aluminium foil is raised, and the positive electrode lead (not shown) is formed.

[0018] (3)  $1 \text{ mol/l}$ . of  $\text{LiPF}_6$  was dissolved in the mixed solvent (EC:MEC=30:70: volume ratio) which consists of preparation ethylene carbonate (EC) and methylethyl carbonate (MEC) of an electrolysis solution, and organic electrolysis liquid was prepared. The organic electrolysis liquid prepared in this way was used as the electrolysis solution x. Subsequently, specified quantity addition of the VC was carried out at this electrolysis solution x. The organic electrolysis liquid which the content of VC prepared here so that it might become 0.05 mass % is used as the electrolysis solution a, The organic electrolysis liquid prepared so that it might become 0.1 mass % was used as the electrolysis solution b, the organic electrolysis liquid

prepared so that it might become 1.0 mass % was used as the electrolysis solution c, the organic electrolysis liquid prepared so that it might become 5.0 mass % was used as the electrolysis solution d, and the organic electrolysis liquid prepared so that it might become 10.0 mass % was used as the electrolysis solution e.

[0019]On the other hand, the carbon dioxide ( $\text{CO}_2$ ) which fully performed desiccation and dehydrating treatment was prepared, and the organic electrolysis liquid in which it was made to dissolve by what this carbon dioxide is blown into the above-mentioned electrolysis solution x for under room temperature ordinary pressure (this is called bubbling) until carbon dioxide was saturated in the electrolysis solution x was prepared. The organic electrolysis liquid prepared in this way was used as the electrolysis solution y. The organic electrolysis liquid which similarly dissolved until carbon dioxide was saturated in the above-mentioned electrolysis solution a, and was prepared is used as the electrolysis solution f, The organic electrolysis liquid which dissolved until carbon dioxide was saturated in the above-mentioned electrolysis solution b, and was prepared is used as the electrolysis solution g, The organic electrolysis liquid which dissolved until carbon dioxide was saturated in the above-mentioned electrolysis solution c, and was prepared is used as the electrolysis solution h, The organic electrolysis liquid which dissolved until carbon dioxide was saturated in the above-mentioned electrolysis solution d, and was prepared was used as the electrolysis solution i, and the organic electrolysis liquid which dissolved until carbon dioxide was saturated in the above-mentioned electrolysis solution e, and was prepared was used as the electrolysis solution j.

[0020]It replaces with the mixed solvent which consists of ethylene carbonate (EC) and methylethyl carbonate (MEC) as a solvent of organic electrolysis liquid, Diethyl carbonate (DEC), propylene carbonate, butylene carbonate, Vinylene carbonate, cyclopentanone, sulfolane, 3-methyl sulfolane, 2,4-dimethylsulfolane, 3-methyl-1,3-oxazolidine 2-one, Gamma-butyrolactone, dimethyl carbonate, butylmethyl carbonate, Ethylpropyl carbonate, butylethyl carbonate, dipropyl carbonate, Simple substances, such as 1,2-dimethoxyethane, a tetrahydrofuran, 2-methyltetrahydrofuran, 1,3-dioxolane, methyl acetate, and ethyl acetate, a binary mixture, or three component mixtures may be used. As a solute of organic electrolysis liquid, replace with  $\text{LiPF}_6$  and  $\text{LiBF}_4$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiAsF}_6$ ,  $\text{Li}(\text{CF}_3\text{SO}_2)_2$ ,  $\text{Li}(\text{CF}_3\text{SO}_2)_3$ ,  $\text{LiCF}_3(\text{CF}_2)_3\text{SO}_3$ , etc. may be used.

[0021](4) Prepared the production occasion, and the negative electrode plate 11 and the anode board 12 which were produced as mentioned above of the nonaqueous electrolyte secondary battery, the separator 13 which consists of fine porous membrane made from polyethylene among these was made to intervene, and it piled up, and wound spirally. Subsequently, after having crushed this so that it might become flat, and producing a prismatic electrode group, this prismatic electrode group was inserted from the opening of the armor can



14. Subsequently, after having arranged the spacer 16 in the upper part of an electrode group, the negative-electrode collecting tab 11a which extends from the negative electrode plate 11 of an electrode group was welded to the inner bottom of the tag block 15c in which it was provided by the obturation object 15. As the positive electrode lead which extends from the anode board 12 of an electrode group was put between the armor can 14 and the obturation object 15 on the other hand, the obturation object 15 has been arranged to the opening of the armor can 14. Subsequently, laser welding of between the peripheral wall of the opening of the armor can 14 and the obturation objects 15 was carried out.

[0022] And after letting the bore in which each electrolysis solution x prepared as mentioned above, a-e, y, and f-j were provided by each tag block 15c pass and pouring in into the armor can 14, each negative pole terminal 15a was welded to each tag block 15c, and was closed. Thereby, design capacity produced square-shaped (thickness: 5-mm, width: 30mm, height: 48mm) lithium secondary battery X, A, B, C, D, E, Y, F, G, H, I, and J by 700mAh, respectively. Here, after facing pouring in each electrolysis solution in the armor can 14 and impregnating an electrode group with an electrolysis solution, in order to carry out defoaming the air bubbles by which it was generated in the crevice between electrode groups in the atmosphere of decompression, the great portion of carbon dioxide ( $\text{CO}_2$ ) dissolved in the electrolysis solution is evaporated. The nonaqueous electrolyte secondary battery using the electrolysis solution x was used as the cell X. Similarly, the nonaqueous electrolyte secondary battery using electrolysis solution a-e was made into cell A-E. The nonaqueous electrolyte secondary battery using the electrolysis solution y was used as the cell Y, and the nonaqueous electrolyte secondary battery using electrolysis solution f-j was made into cell F-J.

[0023] 3. a cycle characteristic examination -- using respectively each cell X, A, and B of these, C, D, E, Y, F, G, H, I, and J, constant current charge was carried out until cell voltage was set to 4.2V by 700-mA charging current at the room temperature (about 25 °C), and constant potential charge was carried out until the current value amounted to 20 mA in the constant voltage of 4.2V. Then, 500 cycle repetition \*\*\*\* calculated the service capacity (mAh) after 500 cycles for the charging and discharging cycle of making it discharge by 700-mA discharge current until cell voltage amounts to 2.5V. Subsequently, when it asked for the ratio of early service capacity and the service capacity after 500 cycles and having been asked as a cycle characteristic, a result as shown in the following Table 1 (with no  $\text{CO}_2$  content in an electrolysis solution) and 2 (they are those with  $\text{CO}_2$  content to an electrolysis solution) was brought.

[0024] Using each of these cells X, A, and B, C, D, E, Y, F, G, H, I, and J, at a room temperature (about 25 °C). By 700-mA charging current, constant current charge was carried out until cell voltage was set to 4.2V, constant potential charge was carried out until the current value amounted to 20 mA in the constant voltage of 4.2V, and the full charge of each of these

cells X, A, and B, C, D, E, Y, F, G, H, I, and the J was carried out. Subsequently, three days neglected each cell X, A, and B after these full charges, C, D, E, Y, F, G, H, I, and J in 80 °C atmosphere. When the increase of stock (high-temperature-batteries bulging) of the cell thickness of each cell X, A, and B after neglect, C, D, E, Y, F, G, H, I, and J was measured, a result as shown in the following Table 1 (with no CO<sub>2</sub> content in an electrolysis solution) and 2 (they are those with CO<sub>2</sub> content to an electrolysis solution) was brought.

[0025]

[Table 1]

電池 種類	電 解 液 の 種 類	初期容量 (mA h)	サイクル 特性 (%)	高温電池膨れ (mm)
X	1M LiPF <sub>6</sub> EC/MEC	700	70	+0.15
A	1M LiPF <sub>6</sub> EC/MEC+VC(0.05%)	700	70	+0.17
B	1M LiPF <sub>6</sub> EC/MEC+VC(0.1%)	700	75	+0.25
C	1M LiPF <sub>6</sub> EC/MEC+VC(1.0%)	700	85	+0.31
D	1M LiPF <sub>6</sub> EC/MEC+VC(5.0%)	685	85	+0.33
E	1M LiPF <sub>6</sub> EC/MEC+VC(10.0%)	640	85	+0.40

[0026]Although the initial service capacity of the cell X additive-free in VC is large, it receives with 700mAh, so that clearly from the result of the above-mentioned table 1, Although the addition of VC follows on increasing and initial service capacity decreases with 685mAh (the cell D whose addition of VC is 5.0%), or 640mAh (the cell E whose addition of VC is 10.0%), on the other hand, it turns out that the cycle characteristic is improving. SEI will be formed in a negative-electrode carbon surface, the side reaction in which an electrolysis solution participates by this SEI will be inhibited, and this will be considered that the cycle characteristic improved, if VC is added to an electrolysis solution. Controlling reduction of initial service capacity, if below 5.0 mass % carries out content of VC which an electrolysis solution is made to contain from these things above 0.1 mass %, since it becomes possible to raise a cycle characteristic, it can be said that it is desirable.

[0027]While the addition of VC added to the electrolysis solution follows on increasing on the other hand and a cycle characteristic improves, it turns out that cell bulging by elevated-temperature neglect becomes large. Although this mechanism is not clear at present, if VC is neglected at an elevated temperature, in order to carry out oxidative degradation of the VC conversely and to generate carbon dioxide (CO<sub>2</sub>), it is presumed that cell bulging becomes large. In order to prevent this, he is trying to make the electrolysis solution in which VC was

dissolved contain carbon dioxide ( $\text{CO}_2$ ) in this invention. The content effect of this carbon dioxide ( $\text{CO}_2$ ) is shown in the result of the following table 2.

[0028]

[Table 2]

電池 種類	電 解 液 の 種 類	初期容量 (mA h)	サイクル 特性 (%)	高温電池膨れ (mm)
Y	1M LiPF <sub>6</sub> EC/MEC +CO <sub>2</sub>	7 0 0	7 0	+ 0 . 0 8
F	1M LiPF <sub>6</sub> EC/MEC+VC (0.05%) +CO <sub>2</sub>	7 0 0	7 1	+ 0 . 0 8
G	1M LiPF <sub>6</sub> EC/MEC+VC (0.1%) +CO <sub>2</sub>	7 0 0	7 6	+ 0 . 0 8
H	1M LiPF <sub>6</sub> EC/MEC+VC (1.0%) +CO <sub>2</sub>	7 0 0	8 6	+ 0 . 0 8
I	1M LiPF <sub>6</sub> EC/MEC+VC (5.0%) +CO <sub>2</sub>	6 8 4	8 6	+ 0 . 1 0
J	1M LiPF <sub>6</sub> EC/MEC+VC (10.0%) +CO <sub>2</sub>	6 4 0	8 6	+ 0 . 1 8

[0029]Although the initial service capacity of the cell Y additive-free in VC is large, it receives with 700mAh, so that clearly from the result of the above-mentioned table 2, Although the addition of VC follows on increasing and initial service capacity decreases like the result of the above-mentioned table 1 with 684mAh (the cell I whose addition of VC is 5.0%), and 640mAh (the cell J whose addition of VC is 10.0%), What (as compared with the result of Table 1, it is decreasing substantially) a cycle characteristic improves and most cell bulging is not increasing on the other hand is understood. This is presumed to be what is depended on the carbonic acid tunic (the organic carbonic acid tunic according [ this carbonic acid tunic ] to VC differs in character) formed when negative-electrode carbon and the electrolysis solution containing carbon dioxide ( $\text{CO}_2$ ) contacted. Whether it makes the electrolysis solution containing VC contain carbon dioxide ( $\text{CO}_2$ ) or does not make this contain, it shows the unrelated thing about initial discharge capacity and a cycle characteristic.

[0030]4. When the examination occasion of a negative electrode carbon material and the electrolysis solution (thing containing VC and  $\text{CO}_2$ ) of this invention were used and the carbon material used for a negative electrode was replaced with, it was examined whether cell bulging would change. Then, the negative electrode plate 11 was first produced like \*\*\*\* except the spacing ( $d_{002}$ ) of the field (002) having used a 0.340 nm ( $d_{002}=0.340\text{nm}$ ) carbon material. The electrode group was produced using this negative electrode plate 11 and the same anode board 12 as \*\*\*\*, and this electrode group was inserted in the armor can 14. Subsequently, the organic electrolysis liquid (1M LiPF<sub>6</sub>EC/MEC+VC(1.0%)+ $\text{CO}_2$ ) which was made to dissolve

CO<sub>2</sub> and was prepared while the content of VC became 1.0 mass % is poured in, Design capacity produced the square-shaped (thickness: 5 mm, width:30mm, height:48mm) nonaqueous electrolyte secondary battery K by 700mAh like \*\*\*\*.

[0031]The negative electrode plate 11 was produced like \*\*\*\* except the spacing ( $d_{002}$ ) of the field (002) having used a 0.347 nm ( $d_{002}=0.347\text{nm}$ ) carbon material. The electrode group was produced using this negative electrode plate 11 and the same anode board 12 as \*\*\*\*, and this electrode group was inserted in the armor can 14. Subsequently, the organic electrolysis liquid (1M LiPF<sub>6</sub>EC/MEC+VC(1.0%)+CO<sub>2</sub>) which was made to dissolve CO<sub>2</sub> and was prepared while the content of VC became 1.0 mass % is poured in, Design capacity produced the square-shaped (thickness: 5 mm, width:30mm, height:48mm) nonaqueous electrolyte secondary battery L by 700mAh like \*\*\*\*.

[0032]500 cycle repetition \*\*\*\* calculated the service capacity (mAh) after 500 cycles for the same charging and discharging cycle as \*\*\*\* using each of these cells K and L. Subsequently, when it asked for the ratio of early service capacity and the service capacity after 500 cycles and having been asked as a cycle characteristic, a result as shown in the following table 3 was brought. After carrying out the full charge of each of these cells K and L, when three days were neglected in 80 \*\* atmosphere and the increase of stock (high-temperature-batteries bulging) of the cell thickness of each cells K and L after neglect was measured like \*\*\*\*, a result as shown in the following table 3 was brought. The result of the cell H (negative electrode carbon material:  $d_{002}=0.336\text{nm}$ , electrolysis solution:1M LiPF<sub>6</sub>EC/MEC+VC(1.0%)+CO<sub>2</sub>) is also collectively shown in the following table 3.

[0033]

[Table 3]

電池 種類	負極炭素材料	初期容量 (mAh)	サイクル 特性 (%)	高温電池膨れ (mm)
H	$d_{002}=0.336\text{nm}$	700	86	+0.08
K	$d_{002}=0.340\text{nm}$	690	84	+0.10
L	$d_{002}=0.347\text{nm}$	620	80	+0.20

[0034]If the spacing ( $d_{002}$ ) of a field (002) is in the cell L which used a 0.347 nm

( $d_{002}=0.347\text{nm}$ ) carbon material for the negative electrode so that clearly from the result of the above-mentioned table 3, it compares with the cells H and K, While the cycle characteristic is falling, it turns out that cell bulging at the time of high temperature preservation is large. If the spacing ( $d_{002}$ ) of a field (002) becomes large to 0.347 nm ( $d_{002}=0.347\text{nm}$ ), this, It is presumed

because the carbonic acid tunic formed when the electrolysis solution which contained carbon dioxide ( $\text{CO}_2$ ) in this carbon material contacts was not fully formed. From this, it can be said that it is preferred that the spacing ( $d_{002}$ ) of a field (002) uses a carbon material of 0.340 nm or less as a carbon material used for a negative electrode.

[0035]5. When the examination occasion of positive-active-material material and the electrolysis solution (VC and thing of  $\text{CO}_2$  content) of this invention were used and the material of positive active material was replaced with, it was examined whether the size of cell bulging would change. Then, the anode board 12 was first produced like \*\*\*\* except having used  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  as positive active material. The electrode group was produced using this anode board 12 and the same negative electrode plate ( $d_{002}=0.336\text{nm}$  carbon material) 11 as \*\*\*\*, and this electrode group was inserted in the armor can 14. Subsequently, the organic electrolysis liquid (1M  $\text{LiPF}_6\text{EC/MEC+VC(1.0\%)+CO}_2$ ) which was made to dissolve  $\text{CO}_2$  and was prepared while the content of VC became 1.0 mass % is poured in, Design capacity produced the square-shaped (thickness: 5 mm, width:30mm, height:48mm) nonaqueous electrolyte secondary battery M by 700mAh like \*\*\*\*.

[0036]The anode board 12 was produced like \*\*\*\* except having used  $\text{LiMn}_2\text{O}_4$  as positive active material. The electrode group was produced using this anode board 12 and the same negative electrode plate ( $d_{002}=0.336\text{nm}$  carbon material) 11 as \*\*\*\*, and this electrode group was inserted in the armor can 14. Subsequently, the organic electrolysis liquid (1M  $\text{LiPF}_6\text{EC/MEC+VC(1.0\%)+CO}_2$ ) which was made to dissolve  $\text{CO}_2$  and was prepared while the content of VC became 1.0 mass % is poured in, Design capacity produced the square-shaped (thickness: 5 mm, width:30mm, height:48mm) nonaqueous electrolyte secondary battery N by 700mAh like \*\*\*\*.

[0037]The anode board 12 was produced like \*\*\*\* except having used the mixed positive active material ( $\text{LiCoO}_2\text{:LiMn}_2\text{O}_4=50:50$ ; mass ratio) of  $\text{LiCoO}_2$  and  $\text{LiMn}_2\text{O}_4$  as positive active material. The electrode group was produced using this anode board 12 and the same negative electrode plate ( $d_{002}=0.336\text{nm}$  carbon material) 11 as \*\*\*\*, and this electrode group was inserted in the armor can 14. Subsequently, the organic electrolysis liquid (1M  $\text{LiPF}_6\text{EC/MEC+VC(1.0\%)+CO}_2$ ) which was made to dissolve  $\text{CO}_2$  and was prepared while the content of VC became 1.0 mass % is poured in, Design capacity produced the square-shaped (thickness: 5 mm, width:30mm, height:48mm) nonaqueous electrolyte secondary battery O by 700mAh like \*\*\*\*.

[0038]500 cycle repetition \*\*\*\* calculated the service capacity (mAh) after 500 cycles for the same charging and discharging cycle as \*\*\*\* using each of these cells M, N, and O.

Subsequently, when it asked for the ratio of early service capacity and the service capacity after 500 cycles and having been asked as a cycle characteristic, a result as shown in the following table 4 was brought. After carrying out the full charge of each of these cells M, N, and O, when three days were neglected in 80 °C atmosphere and the increase of stock (high-temperature-batteries bulging) of the cell thickness of each cells K and L after neglect was measured like \*\*\*\*, a result as shown in the following table 4 was brought. The result of the cell H (positive active material:  $\text{LiCoO}_2$ , electrolysis solution:  $1\text{M LiPF}_6/\text{EC}/\text{MEC}+\text{VC}(1.0\%)+\text{CO}_2$ ) is also collectively shown in the following table 4.

[0039]

[Table 4]

電池種類	正極活物質材料	初期容量 (mAh)	サイクル特性 (%)	高温電池膨れ (mm)
H	$\text{LiCoO}_2$	700	86	+0.08
M	$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$	740	82	+0.11
N	$\text{LiMn}_2\text{O}_4$	600	84	+0.12
O	$\text{LiCoO}_2+\text{LiMn}_2\text{O}_4$	650	86	+0.08

[0040] Even if it uses  $\text{LiCoO}_2$  as positive active material so that clearly from the result of the above-mentioned table 4, Even if it uses  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  as positive active material, Whether it uses  $\text{LiMn}_2\text{O}_4$  as positive active material or uses the mixture of  $\text{LiCoO}_2$  and  $\text{LiMn}_2\text{O}_4$  as positive active material, it turns out that the size of a cycle characteristic and cell bulging at the time of high temperature preservation does not change so much. Although initial service capacity changes with the kinds of positive active material, this is based on the theoretical capacity of each positive active material. If the electrolysis solution of this invention is used from this no matter what positive active material it may use, it can be said that it is effective.

[0041]

[Effect of the Invention] He is trying to pour in the nonaqueous electrolyte in which dissolved vinylene carbonate and carbon dioxide was made dissolved in the armor can 14 in the nonaqueous electrolyte secondary battery 10 of this invention, as mentioned above. For this reason, when such an electrolysis solution is poured in in the armor can 14, the carbon material of the negative electrode plate 11 will contact the carbon dioxide dissolved in the electrolysis solution, and the coat of carbonic acid will be formed in the carbon surface of the negative electrode plate 11. If this cell is charged, the tunic of organic carbonic acid will come to be shortly formed in the surface of the negative electrode plate 11 of vinylene carbonate. Thereby, even if it saves this nonaqueous electrolyte secondary battery 10 at an elevated

temperature (neglect), it can control that oxidative degradation of the vinylene carbonate which dissolved in the electrolysis solution is carried out by operation of these tunics. As a result, cell bulging can be prevented from arising even if it saves the nonaqueous electrolyte secondary battery 10 at an elevated temperature (neglect).

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[Translation done.]

\* NOTICES \*

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- 2.\*\*\*\* shows the word which can not be translated.
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CLAIMS

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[Claim(s)]

[Claim 1]A negative electrode containing negative electrode active material which consists of a carbon material characterized by comprising the following in which insertion and desorption from a lithium ion are possible, A manufacturing method of a nonaqueous electrolyte secondary battery which is provided with a separator which isolates anodes containing positive active material in which insertion and desorption from a lithium ion are possible, and these anodes and negative electrodes in an armor can, and pours in and forms nonaqueous electrolyte in this armor can.

A vinylene carbonate melting process which dissolves vinylene carbonate in nonaqueous electrolyte.

A carbon dioxide dissolved process of making carbon dioxide dissolved in nonaqueous electrolyte in which said vinylene carbonate was dissolved.

A pouring-in process of pouring in nonaqueous electrolyte in which said vinylene carbonate was dissolved and carbon dioxide was dissolved in said armor can.

[Claim 2]A manufacturing method of the nonaqueous electrolyte secondary battery according to claim 1 characterized by making it make this carbon dioxide dissolved in this nonaqueous electrolyte by blowing carbon dioxide into nonaqueous electrolyte in which said vinylene carbonate was dissolved by ordinary temperature ordinary pressure in said carbon dioxide dissolved process.

[Claim 3]A negative electrode containing negative electrode active material which consists of a carbon material in which insertion and desorption from a lithium ion are possible, A separator which isolates anodes containing positive active material in which insertion and desorption from a lithium ion are possible, and these anodes and negative electrodes, Are nonaqueous electrolyte the nonaqueous electrolyte secondary battery which it had in an armor can, and in



said negative electrode surface. A nonaqueous electrolyte secondary battery, wherein a coat formed when carbon dioxide dissolved in said nonaqueous electrolyte at least was contacted, and a tunic formed of vinylene carbonate which dissolved in this nonaqueous electrolyte at the time of charge of this nonaqueous electrolyte secondary battery are formed.

[Claim 4] A negative electrode containing negative electrode active material which consists of a carbon material in which insertion and desorption from a lithium ion are possible, While being the nonaqueous electrolyte secondary battery provided with a separator which isolates anodes containing positive active material in which insertion and desorption from a lithium ion are possible, and these anodes and negative electrodes, and nonaqueous electrolyte in an armor can and containing vinylene carbonate, A nonaqueous electrolyte secondary battery using nonaqueous electrolyte in which carbon dioxide was made dissolved to saturation.

[Claim 5] The nonaqueous electrolyte secondary battery according to claim 3 or 4, wherein content of vinylene carbonate which dissolved in said nonaqueous electrolyte is 0.1 to 5.0 mass % to mass of this electrolysis solution.

[Claim 6] The nonaqueous electrolyte secondary battery according to any one of claims 3 to 5 with which said carbon material is characterized by a spacing ( $d_{002}$ ) of a field (002) being a carbon material of 0.340 nm or less.

[Claim 7] The nonaqueous electrolyte secondary battery according to any one of claims 3 to 6, wherein said anode uses  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ , and  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  and  $\text{LiMn}_2\text{O}_4$  or these mixtures as the main ingredients.

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[Translation done.]

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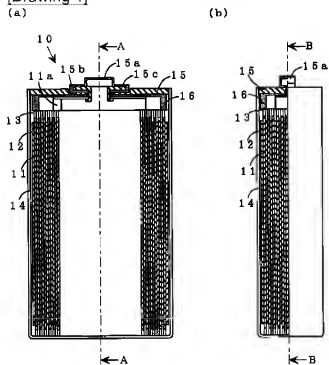
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DRAWINGS

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[Drawing 1]



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[Translation done.]